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TECHNICAL MEMORANDUM

Evaluation of Ebullition Potential to Transport Non-Aqueous Phase Liquids in the Gowanus Canal

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The facilitated migration of non-aqueous phase liquid (NAPL) from sediment to the overlying surface water via ebullition has been documented at several sites containing NAPL-impacted sediment (McLinn and Stolzenburg, 2009). The conceptual site model (CSM) for the Gowanus Canal identified ebullition as a potential migration pathway for NAPL transport within the canal. Several studies performed for the Gowanus Canal indicate the prevalent occurrence of gas production as a result of decaying organic matter found in the underlying sediments. As an example, a report prepared for the New York City Department of Environmental Protection (NYCDEP) in 1993 noted that ebullition was occurring and that, "Organics that settle into the sediment and decay produce gases that escape and either oxidize in the water column or release into the atmosphere" (HydroQual, 1993). Ebullition events in the canal have been observed and documented and provide further validation of this migration pathway.

In order to better understand how ebullition affects the potential for NAPL migration in the Gowanus Canal, CH2M HILL performed a literature review and subsequent data evaluation. This technical memorandum presents the findings of that evaluation.

Background

Several site characteristics of the Gowanus Canal are important to understand when evaluating the impact of ebullition at this site. First, the material underneath the canal is composed of two types of sediment, referred to hereinafter as "soft" and "native" sediment. The soft sediments represent the first 1 to 20 feet (average of 10 feet) of sediment, directly below the water-sediment interface, with the thickest portions at the head of the canal and the turning basins. These sediments were, and continue to be, deposited above the native sediments after canal construction, have a high organic content, and are composed of a sand-silt-clay mixture. The high organic content is largely a result of historical and current combined sewer overflows (CSOs), which have been noted in several reports and various studies of the Gowanus Canal. A study performed for NYCDEP in 1993 found that "the upper 500 feet of the Canal are most effected by outfall solids" (HydroQual, 1993). The native sediments are directly below the soft sediment and are the alluvial and marsh deposits from the Gowanus Creek that were left after construction. Native sediments consist of sands, silts, silty sand, sandy clay, clay, and peat. (U.S. Environmental Protection Agency, 2011)

Second, the Gowanus Canal has varying levels of contamination and has been divided into four remediation target areas (RTAs) or "reaches" (1, 2, 3a, and 3b) based on the following factors: the degree of NAPL contamination in sediments, the navigational requirements for specific sections of the canal, and a comparison of chemical concentrations in soft and native sediments to risk-based preliminary remediation goals. The RTAs are shown in Figure 1. The details of the RTAs are summarized in Table 1, and average sediment profiles for each RTA are shown in Figure 2.

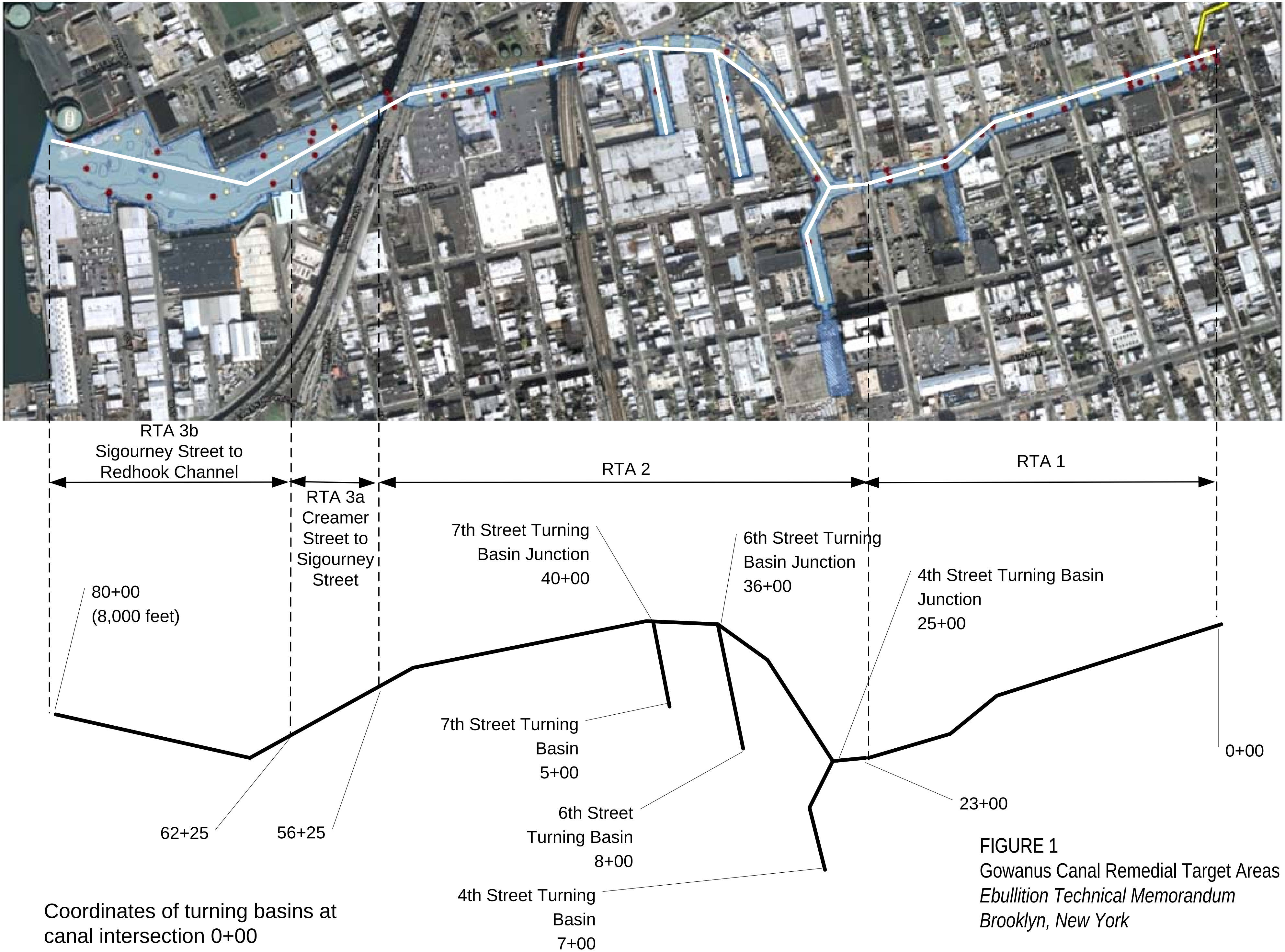

FIGURE 1
Gowanus Canal Remedial Target Areas
Ebullition Technical Memorandum
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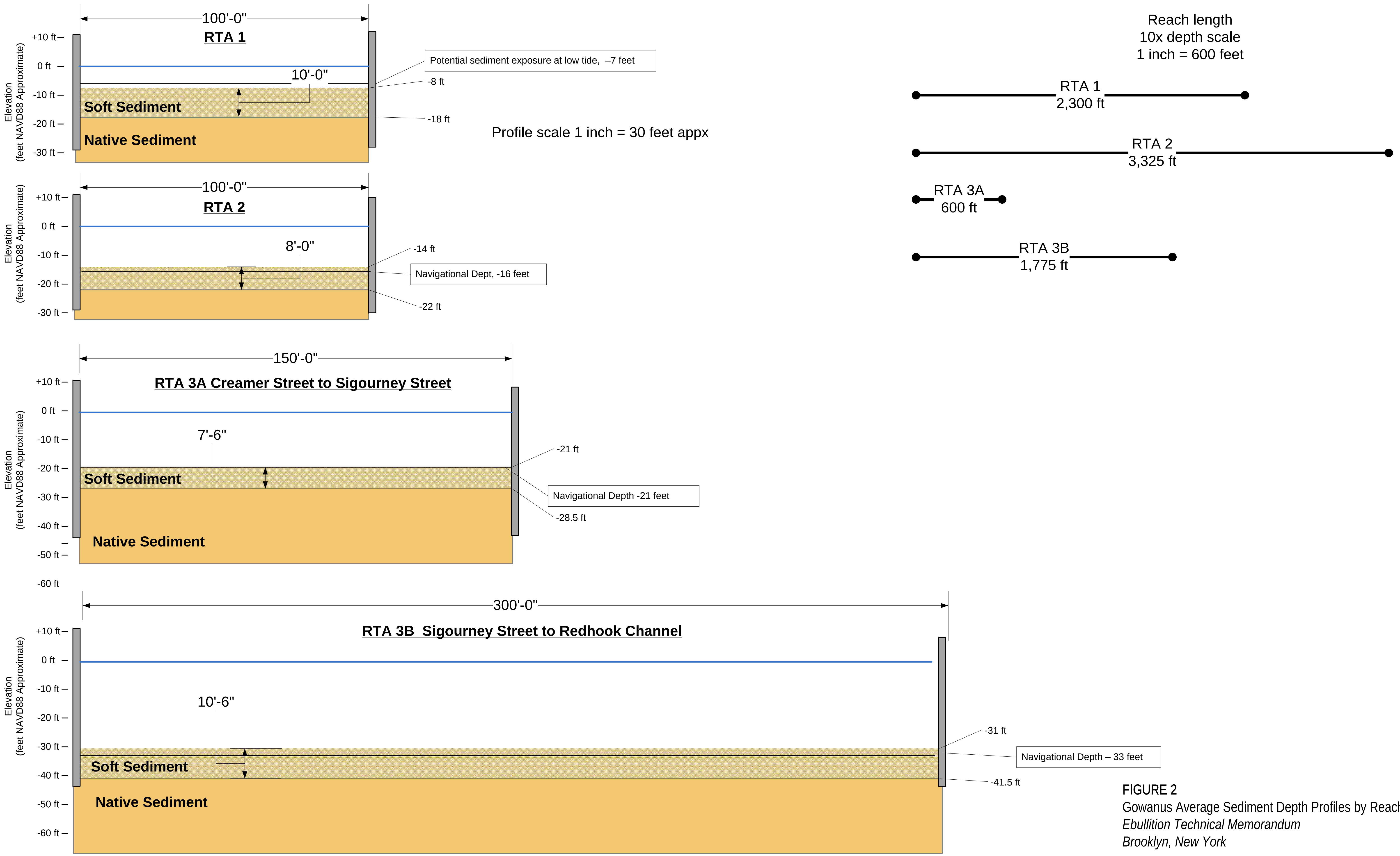

FIGURE 2
Gowanus Average Sediment Depth Profiles by Reach
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TABLE 1
Summary of RTA Characteristics

Characteristics	**RTA 1 – Upper Canal** **From Head of Canal to 3rd Street** **(STA 0+00 to 23+00)**	**RTA 2—Middle Canal** **Between 3rd and Creamer Streets** **(STA 23+00 to 56+25), Including 4th, 6th, 7th, and 11th Street Turning Basins***	**RTA 3A—Lower Canal** **Creamer Street to Sigourney** **Street (STA 56+25 to 62+25)**	**RTA 3B—Lower Canal** **Sigourney Street to Redhook** **Channel (STA 62+25 to 80+00)**
Water Depth [feet (ft) and meters (m)]	0-to-16 ft [0 to 4.88 m]	8-to-20 ft [2.44 to 6.1 m]	12-to-30 ft [3.66 to 9.14 m]	28- to 34 ft [8.53 to 10.36 m]
Canal Width (feet)	Approximately 100	Approximately 100	Ranges from approximately 75 to 225	Ranges from approximately 225 to 600
Length of Canal (feet)	Approximately 2,300	Approximately 3,325	Approximately 600	Approximately 1,775
Canal Usage	No commercial navigation and limited recreational navigation	Light commercial and recreational navigation	Significant commercial and recreational navigation	Significant commercial and recreational navigation
CSO Outfalls	5 CSO outfalls	3 CSO outfalls	1 CSO outfall	1 CSO outfall
Degree of Contamination in Soft Sediment	Moderate level of soft contamination compared to the other reaches. The upper canal soft sediments showed fewer NAPL impacts than the middle canal. Only a few samples in the vicinity of the flushing tunnel had NAPL in the soft sediments.	Highest level of soft sediment contamination compared to the other reaches. The soft sediments in the middle canal are contaminated by NAPL or contain free product, particularly in the areas directly in front of the two former manufactured gas plant (MGP) sites located along this reach. The NAPL impacts near the Carroll Gardens/Public Place former MGP site appear to be more significant than the impacts near the Metropolitan former MGP site. Additional pockets of NAPL impacts and free product are also present in areas between the two former MGP sites.	Relatively lower sediment contamination compared to the other reaches. The NAPL impacts in soft sediment are limited in the lower canal. Only a few samples scattered along the length of this reach had visual evidence of NAPL impacts.	Relatively lower sediment contamination compared to other reaches. The NAPL impacts in soft sediment are relatively infrequent in the lower canal.
Degree of Contamination in Native Sediment	Nearly all the native sediments in the uppermost portion of the upper canal showed NAPL impacts, with native sediment samples all	The native sediment in this reach is heavily contaminated, with nearly all samples containing free product.	The native sediments showed some NAPL impacts, but none showed evidence of free product.	The native sediments showed some NAPL impacts, but none showed evidence of free product.

TABLE 1
Summary of RTA Characteristics

Characteristics	RTA 1 – Upper Canal From Head of Canal to 3rd Street (STA 0+00 to 23+00)	RTA 2—Middle Canal Between 3rd and Creamer Streets (STA 23+00 to 56+25), Including 4th, 6th, 7th, and 11th Street Turning Basins*	RTA 3A—Lower Canal Creamer Street to Sigourney Street (STA 56+25 to 62+25)	RTA 3B—Lower Canal Sigourney Street to Redhook Channel (STA 62+25 to 80+00)
	along the reach containing free product.			

Note:

* The 4th, 6th, 7th, and 11th Street turning basins are included in RTA 2 because they are assumed to have the same navigational use requirements as the main canal in this reach.

Overview of Gas Ebullition

Ebullition, as defined by Merriam-Webster, is “the act, process, or state of boiling or bubbling up”. As related to environmental transport, ebullition is the natural process whereby methane and other gases generated from biodegradation of organic matter are released from water bodies via gas bubbles. Sediments with a high organic content typically are anoxic below the first several millimeters of sediment (Torres et al., 2011). In anaerobic conditions such as these, methanogenisis is a common microbial degradation type (Zeikus and Winfrey, 1976). The biogenic gas bubbles generated by methanogenisis typically consist of methane, nitrogen, and trace amounts of other molecules (Kavcar, 2008). As measured by McLinn and Stolzenburg (2009) at an MGP tar site, measured gas bubble concentrations can range from 50 to 90 percent methane, 0.3 percent carbon dioxide, and 34 to 50 percent other (likely nitrogen and volatile organic compounds). As these bubbles rise to the surface, the occurrence can appear as if the water is boiling, from which the term was derived.

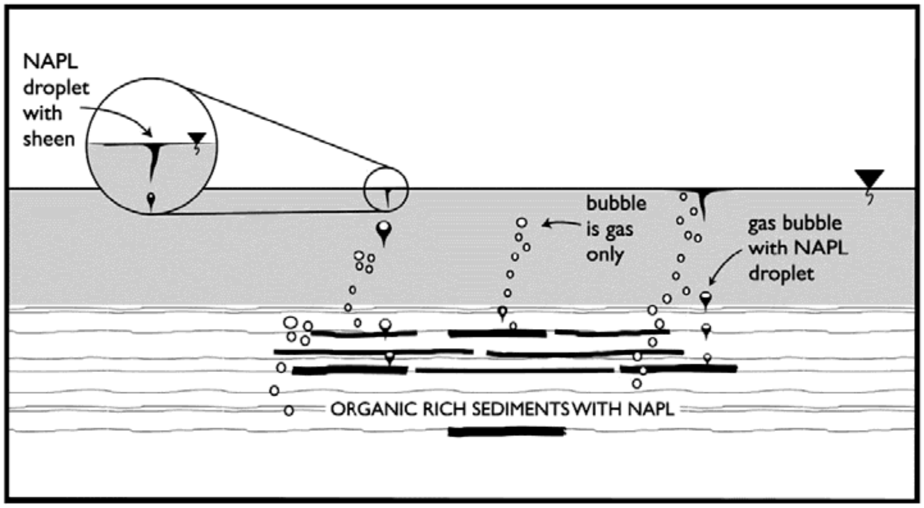
In environments such as the Gowanus Canal that have NAPL-containing, organic-rich sediment, the gas bubbles can serve as a significant transport mechanism of the hydrophobic NAPL to the overlying surface water. This transport mechanism has been observed at the following sites (McLinn and Stolzenburg, 2009):

- St. Louis River/Interlake/Duluth Tar Superfund Site, Minnesota
- McCormick and Baxter Creosoting Superfund Site, Oregon
- Thea Foss Waterway portion of the Commencement Bay Superfund Site, Washington
- Pine Street Barge Canal Superfund Site, Vermont
- Bubbly Creek in Illinois

Figure 3 illustrates how hydrophobic NAPL droplets can coat the gas bubbles (sometimes NAPL is entrained within the bubble) and then get carried to the surface. Once on the surface, the bubbles either burst, creating a sheen, or remain on the surface until enough gas escapes to make the droplet more dense than water again and then sink to the sediment floor, thereby contaminating the sediment surface.

Figure 4 shows an ebullition sheen observed on the Gowanus Canal.

FIGURE 3
Ebullition in NAPL Contaminated Sediments



Source: Figure borrowed from McLinn and Stolzenber,g 2009

FIGURE 4
Ebullition Sheen at Gowanus Canal (RTA 2)

Factors Affecting Gas Ebullition

Several environmental conditions and triggers affect ebullition. However, as observed by McLinn and Stolzenburg in 2009, it is the combination of multiple environmental factors that drive the gas generation of ebullition. Furthermore, the transport of the generated gas bubble to the surface and then its ultimate fate is dependent on additional conditions. Each of these factors has been the subject of at least one ebullition study. Table 2 summarizes these conditions and triggers and lists some of the associated studies.

TABLE 2
Environmental Conditions Affecting Ebullition

Environmental Conditions	Effect	Triggers	Study
Temperature	Affects microbial activity within sediment and gas saturation concentration	Seasonal changes Water depth (can be tidally influenced) Sediment depth	Various sites as listed in McLinn and Stolzenburg, 2009. Viana et al. 2012 Kavcar, 2008
Hydrostatic pressure over water body	Affects gas solubility and bubble size	Water depth (can be tidally influenced)	Various sites as listed in McLinn and Stolzenburg, 2009. Joyce and Jewell 2003. Ostrovsky et al.
Atmospheric Pressure	Affects gas solubility and bubble size	Weather changes such as pressure fronts	Yuan et al.
Total Organic Content (TOC)	Affects microbial activity	Velocity of overlying water body	Viana et al., 2012
Redox Conditions	The oxidation/reduction potential affects the type and rate of biodegradation. In anaerobic conditions methonogenesis occurs in strongly reducing conditions.	Transient groundwater discharges can change redox condition	U.S. Geological Survey, 2006
Sediment Strength	Affects gas migration	Degradation of organics, changing pressure, and tidal influence	McLinn and Stolzenburg, 2009
Water Depth	Affects accumulation of organic matter Affects formation and migration of gas bubbles	Tidal Influence	McLinn and Stolzenburg, 2009 Joyce and Jewell, 2003
Bottom Currents	Affects accumulation of organic matter. Affects shear strength of sediments and release of bubbles	Wind, bathymetry, pressure	Joyce and Jewell, 2003

Table 2 illustrates that there are several potential factors that affect ebullition. However, a few of these factors have a greater impact and can influence whether ebullition occurs. Total organic content of the sediment will affect what level of microbial activity occurs and how much potential gas flux can occur from that sediment.

Viana et al. (2012) described the following simple linear relationship between gas flux, temperature and organic carbon:

$$\mathbf{GF_m = 8.9T + 3.0OC}$$

Where, $\mathbf{GF_m}$ = molar gas flux (mmol m^{-2} d^{-1}), **T** = sediment temperature (°C), **OC** = organic carbon (typically based on surface concentrations).

This equation suggests that organic carbon is a primary contributor to the potential for sediment ebullition and that the rate increases threefold based on the organic content.

In addition to TOC, temperature (water and sediment temperature), greatly affects gas flux, as shown in the equation. This temperature dependence was the subject of several of the studies reviewed. McLinn and Stolzenburg (2009) observed greater migration of tar from sediments to surface water by ebullition when river temperatures ranged from 15 to 24 degrees Celsius (^oC). A third crucial factor is water depth. Water depth influences the temperature of the sediments; higher temperatures would be associated with shallower water depths. Water depth also influences methane flux due to change in solubility with change in hydrostatic pressure (Joyce and Jewell, 2003). Additionally, the depth of the water body affects the quality of organic material that reaches the sediments. In deeper zones, due to prolonged settling time, organic matter undergoes decomposition in the water column, resulting into less labile and more refractory organic matter (Torres et al., 2011). Water depths of more than 5 to 6 meters (16.4 to 19.7 feet) have been observed to have minimal ebullition affects (Joyce and Jewell, 2003; McLinn and Stolzenburg, 2009).

Data Evaluation

Information obtained from the literature search was applied to the site-specific information and data from the Gowanus Canal. Table 3 shows the average percent TOC by canal reach in both the native and soft sediment and the ebullitive potential of soft sediment compared to native sediment using the basic relationship described by Viana et al. above.

TABLE 3
Average Percent TOC and Ebullitive Potential by Remedial Target Area

RTA	Native Sediments Average %TOC	Soft Sediments Average %TOC	Ebullitive Potential of Soft Sediment vs. Native Sediment
1	1.3	11.0	8.5 times greater
2	2.4	14.8	6.2 times greater
3A	2.1	9.8	4.7 times greater
3B	0.4	5.9	15 times greater

Table 3 shows that based on the average percentage of TOC in the soft sediments, the ebullitive potential is 4.67 to 15 times greater in the soft sediment than in the native sediment.

In addition to this analysis, each reach of the canal was evaluated against several factors that were discussed above and shown to affect ebullition. Table 4 presents the following factors: TOC, sediment temperature, water depth, proximity to water interface, and NAPL impacts. These factors as they pertain to the Gowanus Canal are summarized in Table 4.

TABLE 4

Gowanus Canal Ebullition Potential by Remedial Target Area

Site Characteristic	Importance	RTA 1	RTA 2	RTA 3A	RTA 3B
TOC	Degradable organic carbon provides the food for the formation of ebullition gases. Higher organic carbon results in higher potential for ebullition gas formation.	**Soft:** Average TOC content from Remedial Investigation (RI) data is 110,000 mg/kg	**Soft:** Average TOC content from RI data is 148,000 mg/kg	**Soft:** Average TOC content from RI data is 98,000 mg/kg	**Soft:** Average TOC content from RI data is 59,000 mg/kg
		Native: Average TOC content from RI data is 13,000 mg/kg	**Native:** Average TOC content from RI data is 24,000 mg/kg	**Native:** Average TOC content from RI data is 21,000 mg/kg	**Native:** Average TOC content from RI data is 3,900 mg/kg
		Conclusion: Higher TOC content of soft sediment (8.5 times more than native) results in much higher ebullition potential. This reach has greater potential than Reach 3A and 3B.	**Conclusion:** Higher TOC content of soft sediment (6.2 times more than native) results in much higher ebullition potential. This reach has greater potential than Reach 3A and 3B.	**Conclusion:** Higher TOC content of soft sediment (4.6 times more than native) results in much higher ebullition potential. This reach has lower potential than Reach 1 and 2.	**Conclusion:** Higher TOC content of soft sediment (15 times more than native) results in much higher ebullition potential. This reach has lower potential than Reach 1 and 2.
Sediment Temperature	Sediment temperature affects microbial activity, gas saturation concentration, and migration of gas and contaminants. Optimum sediment temperatures for methanogenesis are 35 to 42 °C (Zeikus and Winfrey, 1976). Greater migration of tar from sediments to surface water by ebullition was observed by McLinn and Stolzenburg (2009) at river temperatures ranging from 15 to 24 °C.	**Conclusion:** Surface water temperatures range from 17.5 °C to 28.2 °C between the months of May and October 2012 (with the peak temperature in August).[a] Sediment temperature data are not available, but is assumed to be close to the average groundwater temperature of 12.8 °C (55 °F). Based on this information, ebullition is likely occurring during much of year, but will vary seasonally and perhaps with the tide.			
Water Depth	Depth of water to sediment affects the hydrostatic pressure realized by the underlying sediments, which in turn affects the gas solubility and bubble size of the ebullition gas. Shallower water results in lower hydrostatic pressure and greater potential for ebullition gas to form. Additionally, lower hydrostatic pressure results in larger bubble sizes, which are more efficient at transporting the ebullition gas to the surface (Ostrovsky et al., 2008). Ebullitive affects have been found to be minimal at water depths of more than 5 to 6m (Joyce and Jewell, 2003 and (McLinn and Stolzenburg, 2009).	**Water Depth:** 0-to-16 ft (0 to 4.88 m)	**Water Depth:** 8-to-20 ft (2.44 to 6.1 m)	**Water Depth**: 12-to-30 ft (3.66 to 9.14m)	**Water Depth:** 28- to 34 ft (8.53 to 10,36 m)
		Conclusion: All water depths within this reach are within the range of depths that are associated with noticeable ebullition.	**Conclusion:** Majority of water depths within this reach are within the range of depths that are associated with noticeable ebullition. Figure 4 presents documented ebullition in this reach.	**Conclusion:** Some of the water depths within this reach are within the range of depths that are associated with noticeable ebullition.	**Conclusion:** None of water depths within this reach are within the range of depths that are associated with noticeable ebullition.
Sediment Thickness/Proximity to Water Interface	Sediment thickness/proximity to water interface affects the microbial activity of the sediment and the likelihood of ebullition. Joyce and Jewell (2009) observed that the upper 10 to 20 cm of the sediment column has the most methane ebullition.	**Soft:** Average of 10 ft thick	**Soft:** Average of 8 ft thick	**Soft:** Average of 7.5 ft thick	**Soft:** Average of 10.5 ft thick
		Native: Native sediment proximity to the surface water interface is dependent on thickness of soft sediment and water depth.			
		Conclusion: Because the upper 10-20 cm of the sediment column has the most methane ebullition, the soft sediment is the primary source of ebullition.			
NAPL Impacts	NAPL impacts are not a likely cause to ebullition, but if present, can be mobilized by ebullition.	**Soft:** 15 percent NAPL impacts	**Soft:** 43 percent NAPL impacts	**Soft:** One percent NAPL impacts	**Soft:** 18 percent NAPL impacts

[a] Source: (http://www.riverkeeper.org/water-quality/locations/nyc-hudson-bergen/gowanus-canal/#bsd)

cm = centimeters

mg/kg = milligrams per kilogram

RI =

Conclusions

As shown in Table 4, ebullition is likely limited to the soft sediment, with RTA 1 and RTA 2 having the highest ebullitive potential based on several of these factors. RTA 1 and RTA 2 had the highest TOC in the canal. Across all four reaches, the TOC in soft sediments was 4.2 to 15 times greater than the TOC in the native sediment. Limited temperature data are available for the sediment and water, and no specific data were found for the different reaches. However, based on surface water temperatures and an assumption for the sediment temperature, ebullition is likely occurring during much of the year, but will vary seasonally and perhaps with the tide. Additionally, because shallower waters can be associated with greater temperatures, RTAs 1 and 2 were scored highest. These scores were directly related to the water depths. Water depths of RTAs 1, 2, and 3A show potential for ebullition, with RTA 1 having the highest potential, followed by RTA 2 and then 3A. Sediment thickness data show that ebullition is likely limited to the soft sediment. NAPL impacts, while not likely triggers for ebullition, are visual indicators of its occurrence and of how much NAPL can be mobilized. RTA 2 is most affected by NAPL, followed by RTAs 3B and 1 (scored equally due to similar results), and then 3A.

Factoring in all of these conclusions, Table 5 qualitatively represents the overall ebullitive potential to transport NAPL for each reach of the soft sediment. Each reach was given a rank of 0 to 4 and then a total score was calculated. RTAs 1 and 2 have the highest ebullitive potential based on this analysis.

TABLE 5
Comparative Ebullitive Potential

Characteristic	RTA 1	RTA 2	RTA 3A	RTA 3B
Soft Sediment TOC	3	4	2	1
Temperature	4	3	1	0
Water Depth	4	3	1	0
Sediment Thickness	0	0	0	0
NAPL Impacts	3	4	1	3
Total	**14**	**14**	**5**	**4**
Ebullitive Potential	Highest and nearly 3 times higher than 3A or 3B		Low	Lowest

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